A CONTRIBUTION TO THE SOLUTION OF THE "PECHMANN DYES" PROBLEM: THE CHEMISTRY OF ACYL PARAQUINONES.

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DISSERTATION

Submitted in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy
in the Faculty of Pure Science
of Columbia University.

BY

HENRY PRICE HOWELLS, B.S. in Chem., M.S.

NEW YORK CITY
1927

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ACKNOWLEDGMENT

Warmest thanks are due to Professor Marston Taylor Bogert, who aided me greatly with his counsel and knowledge.

Henry P. Howells.

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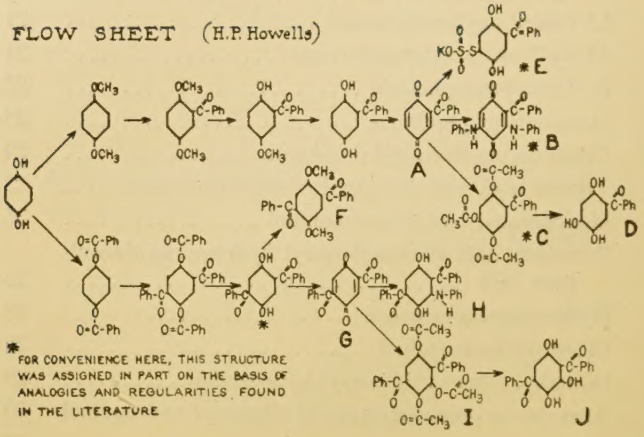

FLOW SHEET (H.P. Howells)
* FOR CONVENIENCE HERE, THIS STRUCTURE WAS ASSIGNED IN PART ON THE BASIS OF ANALOGIES AND REGULARITIES FOUND IN THE LITERATURE.

A CONTRIBUTION TO THE SOLUTION OF THE "PECHMANN DYES" PROBLEM: THE CHEMISTRY OF ACYL PARAQUINONES.

ABSTRACT OF THE DISSERTATION.

A. WHAT WAS ATTEMPTED AND WHY.

1. To furnish additional support to the work of Bogert and Ritter,[27] in which they pointed out that the diaroyl p-quinone structure proposed by Kozniewski and Marchlewski[18] for the "Pechmann Dyes" was not in agreement with the facts, and submitted evidence that the simplest Pechmann dye was the transdilactone of diphenacylmaleic acid.

(1) The synthesis of symmetrical dibenzoyl p-quinone and a detailed study of its properties.

(2) The study of the chemical behavior of the hitherto unknown acyl p-quinones with particular reference to the general effect of acyl substituents on the properties of the quinone nucleus.

2. To develop along certain interesting lines the use of acyl p-quinones as potential dyestuffs.

METHOD OF ATTACK AND RESULTS.

1. In order to obtain the acyl p-quinones described herein in sufficient amounts to warrant further study, it was necessary to carry out a preliminary study of methods for introducing benzoyl groups into the nucleus of hydroquinol.

2. Monobenzoyl hydroquinol was obtained in good yields by a greatly improved method, which involved the use of the Friedel and Crafts reaction, starting with the dimethyl ether of hydroquinol and treating it with benzoyl chloride and anhydrous aluminum chloride in carbon disulfide, then demethylating in two steps by a new process, the only one so far described that proved satisfactory.

3. Dibenzoyl hydroquinol was prepared by a slightly improved method, which involved the careful addition of small amounts of anhydrous aluminum chloride to a mixture of the dibenoate of hydroquinol in benzoyl chloride at a temperature near 200°. Attempts to establish definitely by experiment the relative positions of the benzoyl groups failed, due principally to our inability to reduce satisfactorily the benzoyl groups to hydrol groups, and to control the bromination of dibenzoyl hydroquinol to produce a dibromo substitution product.

4. Monobenzoyl and dibenzoyl hydroquinol were oxidized in the cold with dilute chromic acid mixtures to give good yields of the corresponding quinones.

5. When monobenzoyl p-quinone was treated in the following manner the results were:

(1) with aniline in glacial acetic acid, beautiful, deep purplish red crystals of a dianilido derivative of monobenzoyl p-quinone formed; (2) with acetic anhydride in the presence of a trace of concentrated sulfuric acid, the triacetate of monobenzoyl hydroxy hydroquinol formed. This was a new means of producing compounds of this type.

6. When dibenzoyl p-quinone was subjected to reactions similar to the above, it condensed with aniline to give a monoanilido derivative of the dibenzoyl hydroquinol, and with acetic anhydride to give the triacetate of dibenzoyl hydroxy hydroquinol. The method used for preparing the latter compound was the only one so far given for producing a disubstituted hydroxy hydroquinol derivative in which the substituents were acyl groups.

7. A somewhat general study has been made of the comparative stability and activity of monobenzoyl and dibenzoyl p-quinones toward various reagents such as alkali, oxidizing and reducing agents. Several unusual and interesting observations in this respect have been pointed out. The possibility of the acyl hydroquinols giving rise to products whose structures resembled beta diketone types, has been suggested as an aid in elucidating certain of the above striking properties. In the case of the corresponding hydroquinols, as well as the hy-

droxy hydroquinols, the introduction of benzoyl groups into the nucleus appeared to produce an increasing stabilizing effect toward oxidation.

8. Dibenzoyl p-quinone was oxidized in the cold by alkaline permanganate or chromic acid mixture to give benzoic acid, and the great ease of these reactions was pointed out as quite in contrast with the more difficult oxidation of the Pechmann dye by the same reagents.

9. Evidence based chiefly upon the chemical behavior of the quinones as listed above, together with their physical properties, has been presented as supporting the conclusions of Bogert and Ritter over and against those of Kozniewski and Marchlewski.

10. The potassium salt of the thiosulfuric acid of monobenzoyl hydroquinol was prepared by treating monobenzoyl p-quinone with sodium thiosulfate, and finally salting out with potassium chloride. The product was condensed with 2-amino-5-dimethyl aniline thiosulfuric acid to give a violet dye.

11. Several experiments to obtain an idea of the tinctorial value of our acyl p-quinones were made. They were shown to possess dyeing properties, but in no case was the color sufficiently fast.

12. The following new compounds were prepared and studied:

A. Monobenzoyl p-quinone.
B. Dianilido monobenzoyl p-quinone.
C. Triacetate of monobenzoyl hydroxyhydroquinol.
D. Monobenzoyl hydroxyhydroquinol.
E. Potassium salt of monobenzoyl hydroquinol thiosulfuric acid.
F. Dimethyl ether of dibenzoyl hydroquinol.
G. Dibenzoyl p-quinone.
H. Monoanilido dibenzoyl hydroquinol.
I. Triacetate of dibenzoyl hydroxyhyroquinol.
J. Dibenzoyl hydroxy hydroquinol.

DISCUSSION.

The present investigation was undertaken primarily with the hope that it might add to the work of Bogert and Ritter[27] in throwing light upon the original work of von Pechmann,[4] in which beta-benzoyl acrylic acid and its homologues were dehydrated by acetic anhydride to give highly colored products, the nature of which was not ascertained, having since been known generally as "Pechmann Dyes." Kozniewski and Marchlewski,[13] twenty-four years later, repeated von Pechmann's work and assigned to these dyes the structures of diaroyl-p-quinones, formed by a dehydration involving the beta hydrogen atom, basing this assumption

$$\begin{array}{l} C_6H_5COC\,|H \\ \quad\|\quad\quad\quad + HO|\,COCH \\ \quad CHCO\,|OH \;+\; \quad H|\,CCOC_6H_5 \end{array} \quad \begin{array}{c} C_6H_5COC\cdot CO\cdot CH \\ \| \quad\quad \| \\ HC\cdot CO\cdot CCOC_6H_5 \end{array}$$

upon the intense color of the compounds, the ease with which they formed di-anils with aniline and benzoic acid on oxidation. In a recent paper, Bogert and Ritter[27] pointed out that the quinone formula was not in harmony with the facts, and submitted evidence that the simplest Pechmann dye was the trans-dilactone of diphenacyl maleic acid.

Although the work of the latter authors left little or no doubt as to the probable structure of the "Pechmann Dyes," the above assumption of Kozniewski and Marchlewski needed more critical examination, particularly since it involved the formation of compounds of a type hitherto unknown, namely diacyl or diaroyl paraquinones. A knowledge of the properties of such quinones would no doubt determine to what extent the original assumptions of these workers were justified.

The importance of a further consideration of the mechanism set forth by Kozniewski and Marchlewski for the dehydration of members of the benzoyl acrylic acid series was also at once realized from the fact that the "Pechman Dyes" so produced were essentially by-products, and the nature of the main products, which were recovered from the reaction mixture, has baffled all previous investigators.

After a survey of the literature early in the course of this work, it appeared that not only had no diacyl p-quinones been prepared, but also that the more simple monoacyl derivatives remained unknown. So the present study was made to cover the more general field of acyl p-quinones, by including the preparation and study of monobenzoyl p-quinone.

Monobenzoyl p-Quinone.

The preparation and subsequent study of this compound appeared at first quite fundamental, in as much as it should prove of value not only as an intermediate step in the formation of the dibenzoyl p-quinone, but also as a much needed guide in a study of the latter substance, which was considerably more difficult to obtain. In this latter connection the results have been most gratifying. As a reasonable method for obtaining monobenzoyl p-quinone, the oxidation of the corresponding hydroquinol was chosen. The preparation of the latter, however, involved essentially the introduction of a benzoyl group into the nucleus of hydroquinol, which task proved to be a surprisingly difficult one.

The methods on record for the introduction of acyl groups into the nucleus of polyphenols have been most successfully and thus extensively applied to resorcinol. Hydroquinol when subjected to the same or similar treatment either failed completely to give the corresponding keto derivatives or gave but small yields usually under much more difficult manipulation. Among the more favorable condensations of this type may be listed the reactions first studied by Doebner and Wolff [1] and then Nencki and Schmid [3]. Doebner and Wolff condensed hydroquinol dibenzoate with two moles of benzoyl chloride in the presence of either anhydrous zinc chloride or aluminum chloride at 190°—200°, and obtained a diketo derivative. Nencki and Schmid in a somewhat similar manner condensed hydroquinol with free fatty acids in the presence of anhydrous zinc chloride. Later, Klinger[21] stated that he had employed benzoic acid and obtained monobenzoyl hydroquinol after the method of Nencki and Schmid, but claimed much less favorable results than when fatty acids were used. The main prod-

uct, other than an unidentified dark colored substance, was reported to be the dibenzoate of hydroquinol. Our experience was much the same as that of Klinger. Klinger and Standke[7] also prepared monobenzoyl hydroquinol by exposing a mixture of p-quinone and benzaldehyde in a sealed tube to sunlight for a long period of time. This reaction was theoretically important but practically it offered little promise as a source of our keto derivative. Thus we were forced to consider other methods that had been used successfully in obtaining such keto derivatives of other polyphenols in the hope that they might be applied to hydroquinol with some degree of success. What appeared to be the most promising of these trials was first the method of Finzi[12] where we heated hydroquinol or its dibenzoate in a nitrobenzene solution with benzoyl chloride in the presence of anhydrous aluminum chloride; and secondly the method of Hoesch [25] where hydroquinol was condensed with benzonitrile in dry ether by means of anhydrous zinc chloride and hydrogen chloride gas. The first reaction failed to yield a keto derivative and only the ethereal salt of hydroquinol was isolated, which was in accordance with the findings of Perrier[8]. He stated that chlorides of fatty acids condensed with phenols, having only one nucleus, in the presence of anhydrous aluminum chloride in carbon disulfide to form keto derivatives, whereas under the same circumstances aromatic acid chlorides formed only ethereal salts. It is interesting to note also that the mono-benzoate of hydroquinol was the sole product of the Hoesch method, even when a large excess of the nitrile was present.

Finally, we availed ourselves of the following indirect method for introducing the benzoyl group into the nucleus of hydroquinol. Kauffman and Grombach[14] prepared 2,5 dimethoxy benzophenone by the Friedel and Crafts reaction starting with the dimethyl ether of hydroquinol. They were unable, however, to demethylate completely their product by refluxing with three parts of constant boiling hydriodic acid, and obtained only 2 oxy, 5 methoxy benzophenone. Herzig and Hofmann[16], two years later, repeated the above demethylation, and succeeded in obtaining the completely demethylated product,

2,5 dioxybenzophenone, when six parts of the hydriodic acid and a very long period of refluxing were used. Their work was repeated here and it was found that the method as described for demethylating completely the dimethyl ether was highly impractical, both from the standpoint of yield of pure product and time consumed. This demethylation problem was solved in the following manner. The first methyl group was removed by anhydrous aluminum chloride in a benzene solution to give 2 oxy, 5 methoxy benzophenone. This was accomplished through a suitable change in the procedure described by Kauffmann and Grombach [14] for the preparation of 2,5 dimethoxybenzophenone. The resulting monomethyl ether was then further demethylated by refluxing with 2½ parts of constant boiling hydriodic acid dissolved in a mixture of glacial acetic acid and acetic anhydride. The reaction was practically complete at the end of one and a half hours. Pregl [28], after an earlier observation of Weishut[23], recommended the addition of a few drops of acetic anhydride or a few crystals of phenol to the hydriodic acid mixture when determining quantitatively the methoxy group in methyl ethers which were very difficult to demethylate. The remarkable influence of these substances in greatly increasing the rate of demethylation has been explained on the basis of the increased solubility effect. In our case cited above, glacial acetic acid was a good solvent and worked well alone, but the addition of a small portion of anhydride seemed to afford a more complete and quicker demethylation. Other than any effect due to increased solubility at a higher temperature, the influence of acetic anhydride in our experiments might have been due to its reaction with the increasingly large proportion of water formed in the operation.

Monobenzoyl p-quinone was obtained from the 2,5 dioxybenzophenone by careful oxidation in the cold with a dilute chromic acid mixture. The product was further characterized by subjecting it chiefly to those reactions which bore particularly upon the original problem under study.

Dibenzoyl p-Quinone.

As in the case of monobenzoyl p-quinone, the most reasonable method for forming this quinone appeared to be through the oxidation of the corresponding hydroquinol. However, we were at once confronted with an almost impossible task of introducing satisfactorily two benzoyl groups into the hydroquinol nucleus. The only case of substitution of this kind found on record, was that of Doebner and Wolff [1], in which the dibenzoate of hydroquinol was condensed with two moles of benzoyl chloride in the presence of small quantities of anhydrous zinc chloride, or better aluminum chloride, at 190°—200°, then with subsequent hydrolysis x, x_1, dibenzoyl hydroquinol resulted. All attempts made here to repeat the work of these authors by following carefully their extremely vague directions led to excessive charring and a yield of pure product in the neighborhood of two per cent of the theoretical. It was not surprising that charring took place to such an extent, in view of the fact that Böeseken[17] found benzoyl chloride to be unstable near 170° in the presence of anhydrous aluminum chloride. We also found this to be the case even at a slightly lower temperature when a longer period of heating was used. It is noteworthy, however, that the apparent decomposition of benzoyl chloride by aluminum chloride was prevented to a considerable degree by keeping the temperature of the reaction as high as possible without materially injuring the desired product, and by making the necessary additions of very small amounts of anhydrous aluminum chloride at wide intervals. Thus the yield of pure product was brought up to 12—15% of the theoretical. Attempts to secure a better method proved fruitless. In this connection it was interesting that two benzoyl groups could not be substituted by the Friedel and Crafts reaction even in steps when 2,5 dimethoxy benzophenone was used as the initial material.

Dibenzoyl p-quinone was obtained by the oxidation of the hydroquinol in a manner but slightly different from that used for preparing monobenzoyl p-quinone, and was further characterized and studied, largely through those reactions which appeared most fundamental in helping solve our problem.

In order to establish the exact structure of dibenzoyl hydroquinol, two ways of approach appeared at first practical. The first was essentially showing through some suitable condensation made between the benzoyl groups, that the latter were, or were not, on adjoining carbon atoms. Should such a condensation not have taken place, then the symmetrical structure of dibenzoyl hydroquinol would have been strongly indicated, since the hydroxyl groups have commonly been demonstrated to have an outstanding tendency over most all other groups in universally directing ortho. It was hoped to have been able to reduce the carbonyl groups to hydrol groups, and then from the results of attempts to eliminate one molecule of water from the dihydrol, to have drawn conclusions as to the relative positions of the original benzoyl groups. Should the hydrol groups have been attached to adjoining carbon atoms, a configuration which would be expected to lose readily a molecule of water should have resulted. Franke and Lieben[24] showed that 1,4 glycols passed readily into gamma oxides or internal ethers by the loss of water.

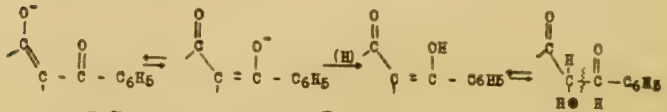
The second method of approach which was chosen in this structure problem was based chiefly on an earlier observation that 2 oxy, 5 methoxybenzophenone underwent an apparent hydrolysis when heated with constant boiling hydrobromic acid in a sealed tube at 135°—140°, and benzoic acid was almost quantitatively produced. Attempts were now made to obtain a dibromo derivative of dibenzoyl hydroquinol, in view of subjecting the same to such treatment as to eliminate the benzoyl groups and form a stable dibromhydroquinol of known structure.

No satisfactory methods for reducing or brominating dibenzoyl hydroquinol to form the desired products were found, and due to the difficulty of obtaining the starting material, further work along this line was suspended.

It has been shown that a benzoyl group in the ortho position to a methoxy group increased greatly the ease of demethylating the latter. Auwers and Rietz[15] pointed out that the monomethyl ether obtained readily by Kauffmann and Grombach [14] from 2,5 dimethoxybenzophenone, and which they

could not demethylate further, was 2 oxy, 5 methoxy benzophenone. Kauffmann[15] in a private communication agreed with these authors, after having shown that the dimethyl ether of o-nitrohydroquinol also had one ether group more easily reduced than the other. It was found here that both of the methoxy groups in the dimethyl ether of dibenzoyl hydroquinol were very readily reduced, which seems to agree with the above observations, should the benzoyl groups occupy positions ortho to different hydroxyl radicals.

It is interesting to note here that when dibenzoyl hydroquinol was suspended in water and treated with three per cent sodium amalgam the main product detected was benzaldehyde. The behavior of the diketone to yield benzaldehyde, much as though an acid chloride were being reduced, appeared somewhat anomalous, and it was thought worthwhile to suggest here a mechanism that might explain it. The blood red color which always developed when the yellow crystals of either mono- or dibenzoyl hydroquinol were dissolved in alkali suggested to us a possible tautomeric change, due to the presence of a carbonyl group and a hydroxyl radical on adjacent carbon atoms. By formulating the change as in [A] and [B], the analogy to the similarly formulated changes commonly offered in the case of beta diketone groupings is obvious. The red color in our experiments may have been due to a quinone structure produced as in [B]. By the reduction of [B] a beta diketone structure would result as in [C] and [D], which should be easily hydrolyzed by alkali to benzaldehyde:



From similar observations to those made on monobenzoyl p-quinone, the dibenzoyl quinone appeared to act as a strong oxidizing agent, possibly even stronger in this respect than the former substance. In this latter connection it appeared interesting to have the reduction potentials of each quinone deter-

mined, in view of striking a parallelism between these measurements and chemical behavior. Conant and others, in recent years, have made quite an extensive and interesting study of the effect of substituents on the reduction potential of the quinone nucleus. Conant [32] reported in a very recent paper that the effect of substituting hydrogen by alkyl groups, as in p-xyloquinone, was to lower the reduction potential to a certain extent, but a similar chlorine substitution raised it. He concluded that the effect of introducing alkyl groups was to diminish the affinity of the quinone molecule for the hydrogen molecule, whereas chlorine increased it regularly, though each subsequent substitution had less effect than the previous one. Judging from a general knowledge of the reactions studied herein, which may be supported by preliminary determinations of the reduction potentials now being planned in this laboratory, the benzoyl group appeared to have similar effect to that of the chlorine atom, which if it be the case would prove most interesting and new for a substituent of this type.

Dibenzoyl p-Quinone and the "Pechmann Dyes"

Kozniewski and Marchlewski[13] prepared what they thought to be the dianilide of symmetrical dibenzoyl p-quinone, by refluxing for several hours one part of the Pechmann dye, obtained from benzoyl acrylic acid, with five parts of aniline in fifty parts of glacial acetic acid. Bogert and Greenberg[31] repeated the work of these authors and extended it to a large number of other amines and obtained beautifully crystalline products having N, N′-substituted aromatic residues. They have thus showed the reaction to be quite general, but have assigned to their products the structure of N, N′-disubstituted dilactams of diphenacyl fumaric acid in agreement with the structure proposed by Bogert and Ritter[27] for the Pechmann dye.

It was of interest here to test the above reaction of Kozniewski and Marchlewski by using in place of their supposed dibenzoyl p-quinone our new quinone which we knew definitely to be a dibenzoyl p-quinone, and thus see if a dianilide would form by the splitting out of two molecules of water between

the carbonyl groups in the quinone nucleus and two molecules of aniline. Aniline was found to react instantly in the cold with our dibenzoyl p-quinone dissolved in glacial acetic acid, and the reaction was apparently complete within a few minutes, giving rise to a monoanilido derivative of dibenzoyl hydroquinol. Apparently the condensation did not take place in the manner assumed by Kozniewski and Marchlewski for a diaroyl p-quinone, and upon which they largely based their proposed structure for the "Pechmann Dyes." Furthermore, since no change in our experiment gave rise to a dianilide of the type suggested by these authors, the structures offered above by Bogert and Greenberg for the products of the condensation of the Pechmann dye with primary amines appear most probable.

Although Kozniewski and Marchlewski did not explain why dibenzoyl p-quinone should be expected to react with aniline to give a dianilide through the splitting out of two molecules of water, it is possible that they may have assumed a similarity between the benzoyl and anilido groups in their effect as substituents in the quinone nucleus. It has been shown that p-quinone condenses with aniline to give first a dianilido derivative which could further be condensed with aniline to an anilide[5] or a dianilide[6].

It is true that the relative positions of the benzoyl groups in dibenzoyl p-quinone were not definitely proved to be symmetrical as in the structure proposed by Kozniewski and Marchlewski for the Pechmann dye, but there is reason to believe that in symmetrical dibenzoyl p-quinone there too the active group would be the quinone nucleus, which should behave, as in addition reactions with aniline, fundamentally in the same manner as our dibenzoyl p-quinone, which very likely may have the symmetrical structure. The present study suggested that the principal nature of the effect produced by the benzoyl groups in the reactions of our acyl p-quinone, was one of degree rather than kind. The quinone nucleus appeared to be the active factor whenever mono- or dibenzoyl p-quinone was subjected to certain condensations, and the latter no doubt followed fundamentally the same mechanism. The fact that

monobenzoyl p-quinone condensed with two molecules of aniline to give a dianilido derivative whereas dibenzoyl p-quinone added apparently but one molecule of aniline to give a monoanilido hydroquinol derivative, should not be taken as indicative of some fundamental difference in the manner of each addition reaction. Such differences in products formed by addition reactions starting with a single quinone, have been commonly accounted for by alternate reduction and oxidation changes. Therefore it is not at all unreasonable to assume here, that when monobenzoyl p-quinone reacted with aniline, alternate reduction and oxidation took place to give rise to dianilido mono-benzoyl p-quinone, whereas dibenzoyl p-quinone added directly one molecule of aniline in essentially the same manner, but subsequent oxidation and reduction was absent.

In order to lend additional support to the assumption that the nature of the addition reactions was essentially the same, each quinone was subjected to the action of acetic anhydride in the presence of a trace of concentrated sulfuric acid in accordance with the method of Thiele[9], used for studying 1,4 addition to unsaturated gamma diketone types. Here any possibility of alternate reduction and oxidation should have been eliminated, and triacetates of the corresponding hydroxyhydroquinols should have resulted, unless the addition reactions of the two quinones differed in some fundamental respect. The triacetates of mono- and dibenzoyl hydroxyhydroquinol were actually obtained. Incidentally the formation of the hydroxyhydroquinol derivatives just mentioned, involved a new means for forming derivatives of these types, and the method is the only one thus far described for producing a disubstituted hydroxyhydroquinol where the substituents are acyl groups. It is noteworthy that dibenzoyl hydroxyhydroquinol dissolved in dilute alkali to give an orange solution which was quite stable toward air oxidation, whereas the monobenzoyl derivative similarly treated gave an orange yellow solution which was oxidized quite readily to a greenish black solution from which none of the original hydroxyhydroquinol could be recovered. This marked increase in stability toward oxidation that was

apparently produced by the introduction of benzoyl groups into the nucleus of hydroxyhydroquinol was in agreement with a similar observation made on the hydroquinol nucleus, making the effect of benzoyl groups appear quite general in this respect.

Further interest was attached here to condensations of dibenzoyl p-quinone with acetic anhydride, since in the dehydration of members of the benzoyl acrylic acid series by acetic anhydride, it was thought that the anhydride might have entered also into an addition reaction with certain unsaturated bodies that were present. An addition with acetic anhydride was suggested in the work of Bogert and Ritter[27] where the product that resulted from the boiling beta-benzoyl alpha-methylacrylic acid with acetic anhydride showed a great increase in weight. Should water have split out from two molecules of benzoylacrylic acid after the assumption of Kozniewski and Marchlewski the quinone so produced might have reacted with the excess acetic anhydride to form a product that remained as the unidentified substance in the reaction mixture. However, the product that formed by the addition of acetic anhydride to our dibenzoyl p-quinone did not in any way resemble the products that were isolated from the dehydration of benzoyl acrylic acid with acetic anhydride.

The above authors obtained benzoic acid by treating the Pechmann dye with hot alkaline permanganate or chromic acid mixture, and used the result also as supporting their proposed quinone structure. Our dibenzoyl p-quinone was oxidized in the cold by the same reagents to give benzoic acid.

The points covered in the foregoing discussion together with the physical properties, support the fact that the properties of the Pechmann dye point to the structure proposed by Bogert and Ritter[27], and not to the quinone formula.[13]

Acyl p-Quinones as Potential Dyestuffs.

Viewed as a possible source of dyestuffs, the acyl p-quinones were of interest, since they possessed the indigo chromophore, –CO·C: C·CO–. The increase in the number of these groups resulting from the introduction of benzoyl groups into

the p-quinone nucleus, seemed to run parallel with an increased change of color toward orange. Although our acyl p-quinones appeared too active chemically to be good dyestuffs in themselves, it was thought that they might possess tinctorial value when applied to wool due to the presence of the amino group in the fibre. In this respect, the amino group of the wool fibre did seem to play an important part.

German patents are on record for the production of thiosulfuric acids[18] from p-quinone and the utilization of the same as potential dyestuffs.[19] The thiosulfuric acid of hydroquinol is described therein as being easily condensed with 2-amino-5-dimethylaniline thiosulfuric acid in alkaline solution by means of air oxidation to give a blue violet dye. For the purpose of effecting a similar condensation, the thiosulfuric acid of monobenzoyl hydroquinol was prepared from monobenzoyl p-quinone and was used to produce a reddish violet dye. This indicated that the acyl p-quinones might be substituted here for p-quinone to give similar dyes possessing somewhat different shades.

EXPERIMENTAL.

1,4 *Dimethoxybenzene*

A slight modification of the method of Ullmann[11] was used in preparing this compound. To a solution of 50 g. of hydroquinol in 275 cc. of 15% sodium hydroxide was added dropwise with constant shaking 105 cc. of methyl sulfate. The temperature was allowed to rise gradually to 50° until most of the methyl sulfate was added. After vigorous agitation of the reacting mixture the remainder of the methyl sulfate was added, and the agitation was resumed for about ten minutes. The excess methyl sulfate was then destroyed by an additional 50 cc. of 10% sodium hydroxide by heating the mixture for an hour on the steam bath. Large flakes of the dimethyl ether separated on cooling, which when filtered, washed, and dried weighed about 60 g. Recrystallization from 75% alcohol gave large, colorless, bright flakes, possessing a powerful, pleasant, ethereal odor, and melting at 56.8°, corr. Yield, about 55.5 g., or 88.5%. Ullman gives 56°.

Introduction of the benzoyl group into the nucleus of hydroquinol.

(1) When hydroquinol was heated with an excess of benzoic acid in the presence of anhydrous zinc chloride, after the method claimed to have been used by Klinger[21], not more than a trace of 2,5 dioxybenzophenone was formed. Hydroquinol dibenzoate was the main product isolated. Mixed M.P. 204°, corr. Klinger gives 200°.

(2) An adaptation of the method of Finzi[12] where hydroquinol, or its dibenzoate, was heated with a slight excess of benzoyl chloride and anhydrous aluminum chloride dissolved in nitrobenzene failed to give a keto derivative. The only product recovered from the black, highly charred liquid was the dibenzoate of hydroquinol. Mixed M.P. 204°, corr.

(3) .1 mole of hydroquinol and .2 mole of benzonitrile and 5 g. of anhydrous zinc chloride in 60 cc. of dry ether were treated with dry hydrogen chloride gas for 5 hours, after an

adaptation of the Hoesch [25] reaction. No keto derivative was obtained, but white, feathery needles of the monobenzoate of hydroquinol separated out. Mixed M.P. 164.5°, corr. Witt and Johnson[9] give 162°—163°.

(4) 2,5 *Dimethoxybenzophenone*; 2 *oxy*, 5 *methoxybenzophenone*, and 2,5 *dioxybenzophenone*. 2,5 dimethoxybenzophenone was made by the method of Kauffmann and Grombach[14] which consisted of treating equal molecular quantities of 1,4 dimethoxy benzene and benzoyl chloride in carbon disulfide with a calculated amount of anhydrous aluminum chloride. The addition product was worked up in the usual manner. To free of unchanged 1,4 dimethoxybenzene and 2 oxy, 5 methoxybenzophenone which was a by-product to the extent of about 10%, it was necessary to carry out long and repeated steam distillations in strong alkali. The yield of pure dimethoxy benzophenone was about 40%. Colorless crystals from methyl alcohol melted at 51.2°, corr. Kauffmann and Grombach gave 51° for yellow crystals, Herzig and Hofmann[16], 50°—52° for colorless crystals.

2-oxy-5-methoxybenzophenone was made the main product in the above by certain important modifications, since it proved to be more easily obtained and was a step nearer the final, desired product. 50 g. of 1,4 dimethoxybenzene and 50 g. of benzoyl chloride dissolved in 50 cc. of carbon disulfide was treated with 60 g. of finely ground anhydrous aluminum chloride, which was added in small portions over a period of 1½ hours, the mixture being maintained at a temperature around 25°. After 48 hours of standing at room temperature, the reaction was further completed by warming for ½ hour at about 50°. The dark resinous mass was decomposed with cracked ice and concd. hydrochloric acid and the yellow product was steam distilled for two hours to free of most of the unchanged dimethylether and carbon disulfide. The resulting brown oil failed to solidify on cooling, so was extracted with ether and dried over fused calcium chloride. The brown oily residue which remained from evaporating the ether was dissolved in 75 cc. of dry benzene and treated with 35 g. of finely ground

anhydrous aluminum chloride, which was added in portions sufficient to maintain a brisk evolution of hydrogen chloride. When the final portion was added, the temperature was gradually raised to the boiling point, and refluxed gently until the evolution of hydrogen chloride ceased. The resulting deep red solution was cooled and then decomposed by 6 N hydrochloric acid. The benzene and the toluene formed in the reaction were removed by steam distillation, leaving the product as a brown oil which on cooling turned to a yellowish colored solid. The crude product when filtered, washed with water, and dried, weighed about 68 g. This was dissolved in a large volume of 70—75% alcohol, and then allowed to cool slowly to room temperature, whereupon a very impure product separated out as a heavy dark oil. 30 g. of fairly pure product was obtained by chilling the decanted supernatant liquid. The impure oily product was dissolved in 10% sodium hydroxide with some difficulty, and the alkaline solution was washed with ether and filtered. The clear red filtrate was acidified until a faint turbidity developed, and the yellow crystalline product was further precipitated by carbon dioxide. Filtered washed with water, and recrystallized from 80% alcohol, to give 20.5 g. of bright yellow plates melting at 84°—85.5°, corr. Yield 50.5 g., or 55%. Kauffmann and Grombach [14] give 78°; Herzig and Hofmann[16], 82°—85°.

2,5 dioxybenzophenone was obtained by demethylating 16 g. of 2 oxy, 5 methoxybenzophenone with 2½ parts of constant boiling hydriodic acid in 20 cc. of glacial acetic acid and 4 cc. of acetic anhydride. The reaction was practically complete at the end of 1½ hours of refluxing. The clear orange colored solution was poured into 100 cc. of cold water, whereupon a yellow crystalline product resulted, which when filtered, washed well with water and dried, weighed about 14.5 g. and melted at 118°—120°. Recrystallization from benzene gave yellow crystals melting at 125°—126.1°, corr. Herzig and Hofmann[16] give 122°—124°; Klinger and Standke[7], 125°. Yield, 13 g., or 87%.

About 5% yields of the same product resulted when the method of Herzig and Hofmann[18] was tried, using 6 parts of constant boiling acid and 12 hours of refluxing.

When constant boiling hydrobromic acid was used in a sealed tube at 130°—140° for 2½ hours, apparent hydrolysis took place to yield mainly benzoic acid together with a red complex material soluble in water.

Monobenzoyl p-Quinone

A solution of 10 g. of 2,5 dioxybenzophenone in 50 cc. of glacial acetic acid was added drop-wise over a period of 20 minutes to a mixture of 8 g. of sodium dichromate and 10 cc. of concd. sulfuric acid in 350 cc. of water, maintaining the temperature around 10°. The mixture was stirred mechanically during the addition and for about ten minutes after until the presence of a dark reddish brown color was very evident. The suspended product was immediately filtered off, washed well with water and dried. Weight about 9 g. The chief impurity seemed to be a trace of benzoic acid. Recrystallization from 500 cc. of ligroin (B.P. 70°—100°) gave 7.5 g. of orange yellow, lustrous, needle-like plates, melting at 85°—85.6°, corr. Yield about 77%.

Great care was exercised in the foregoing recrystallization. To prevent the forming of a dark brown difficulty soluble residue on the bottom of the heated vessel, it was necessary to add the crude product as a fine powder to boiling ligroin which was continually agitated.

The quinone was soluble in most of the common organic solvents, and slightly in hot water, although the latter seemed to have a deleterious action, giving a reddish colored solution. It was attacked by dil. alkali to give a brownish colored solution, from which a light brown flocculent material containing some benzoic acid precipitated out upon acidification. The quinone was easily reduced to the original hydroquinol by means of sulfurous acid. Chemical properties and analysis indicated it to be monobenzoyl p-quinone.

Analysis: Calc. for $C_{13}H_8O_3$, C, 73.57%; H, 3.81%.
Found C, 73.47%; H, 3.83%.

Reaction with hydroxylamine.—The usual manner for obtaining oxime derivatives by condensing in alcoholic solution ketones with hydroxyl amine which is liberated by a calculated amount of base such as sodium carbonate, or acetate, was not successful here. A fugitive purple appeared on first admixture, then a red developed which soon transposed to a reddish brown, such color changes being quite typical of complex couplings involving consecutive oxidation-reduction.

Inasmuch as hydroxylamine is quite prone to act as a reducing agent, especially if a trace of alkali is present, it was deemed advisable to use the hydrochloride salt as such at ordinary temperature over a long period of standing. After 24 hours, the original red mixture became darker and deposited a very small amount of red powder. More of this red amorphous material together with a small amount of crystalline material was thrown out of solution upon dilution with water. A separation of the two was made with difficulty by means of hot dilute alcohol. A small amount of cream colored needles resulted, melting at 99°—99.6° corr.

Dianilido Monobenzoyl p-Quinone

This substance was prepared by a method similar to that used by Zincke and Hagen[5] for preparing simultaneously the dianilido and dianilido anilide of p-quinone. 2 g. of aniline in 4 cc. of glacial acetic acid was added to 1.6 g. of monobenzoyl p-quinone in 20 parts of warm glacial acetic acid. The mixture immediately became deep red, but did not deposit any crystalline material even after a few minutes of additional warming and ½ hour of standing at room temperature. Agitation, however, was now sufficient to commence the crystallizing out of a deep purplish red product, which was complete within one hour. The crystals when filtered, washed with glacial acetic acid and then alcohol, and dried, appeared as small, glittering, purplish red plates, and weighed about 1.2 g. M.P. 210.5°—211.7°, corr.

Recrystallization from a large volume of alcohol gave diamond shaped plates that appeared red by transmitted light and purple by reflected light. M.P. 211.7°—212.2°, corr. Clusters

of small purplish red plates formed from a small volume of hot benzene. M.P. 212.2°—212.7°, corr. Yield about 1 g., or 34%. The product was unaffected by hot sulfurous acid, and no acetylation was observed by heating with acetic anhydride and fused sodium acetate, which was quite characteristic of a dianilide.[9] It dissolved slowly in concd. sulfuric acid to give a deep red coloration, but was insoluble in dilute acid and alkali. Chemical properties and analysis indicated a dianilido derivative of monobenzoyl p-quinone.

Analysis: Calc. for $C_{25}H_{18}N_2O_3$, C, 76.09%; H, 4.60%.
Found C, 76.17%; H, 4.62%.

Triacetate of monobenzoyl hydroxyhydroquinol

An adaptation of the method of Thiele[10] for effecting 1,4 addition of acetic anhydride to unsaturated gamma diketones was found to produce good results with monobenzoyl p-quinone acting as the unsaturated diketone. 2 g. of the quinone was introduced into 6 g. of acetic anhydride to which 3 drops of concd. sulfuric acid had been added. The reaction was completed by warming 2—3 minutes at 40°—50°, whereupon the yellow solution gradually turned almost colorless. The clear mixture was poured into cold water and allowed to stand until all of the excess anhydride was decomposed. A colorless product resulted, which when filtered off, washed well with water, and dried, weighed about 1.4 g. and melted at 135°—137°, corr., indicating the reaction to be practically quantitative. Recrystallization from alcohol gave 1.1 g. of pure, shiny white needles, melting at 137.7°, corr.

The product was insoluble in cold .5 N alkali, but in the hot gave a greenish black solution, apparently due to hydrolysis with subsequent oxidation. All attempts to convert the triacetate into the trimethyl ether and thus compare the same to the 2,4,5 trimethoxy benzophenone of Bargellini and Martegiani[22] failed. Methyl sulfate and alkali were the reagents used, and the hydrolyzed product appeared to be unstable in this system.

Analysis: Calc. for $C_{19}H_{16}O_7$, C, 64.03%; H, 4.53%.
Found C, 63.86%; H, 4.53%.

Monobenzoyl hydroxyhydroquinol

2 g. of the above triacetate was dissolved in 20 cc. of absolute alcohol saturated with dry hydrogen chloride, and the mixture was refluxed for about 2 hours. The alcohol and ethylacetate were then evaporated off under diminished pressure, leaving a reddish colored oil which did not solidify on cooling. The oil was congealed to a yellow crystalline mass by shaking with cold water. The product when filtered, washed well with water, and dried, weighed about 1.3 g. and melted at 128°—129°, corr. Recrystallization from a mixture containing equal parts of benzene and ligroin (B.P. 70°—100°) gave fine orange yellow crystals which melted at 129.1°, corr. Yield, 1 g., or 77%.

The product dissolved in dilute alkali to give a reddish orange solution which turned greenish black after a short exposure to air. Acidification precipitated the original hydroxyhydroquinol from the orange solution, but did not from the greenish black one. The skin was stained rather fast black by the yellow product.

Analysis: Calc. for $C_{13}H_{10}O_4$, C, 67.84% ; H, 4.38%.
Found C, 68.00% ; H, 4.45%.

Potassium salt of monobenzoyl hydroquinol thiosulfuric acid

An adaptation of a briefly described patented process[18] was used for making this new thiosulfuric acid derivative. 5 g. of monobenzoyl p-quinone was dissolved in about 28 cc. of warm glacial acetic acid, and the mixture while at 40°—50° was allowed to flow into a solution of 9 g. of sodium thiosulfate in an equal weight of water. During the reaction the temperature was not allowed to rise more than a few degrees. After 2 hours of standing at room temperature the clear yellow solution had deposited a small amount of a fine yellow solid, which was filtered off and identified by a mixed melting point to be 2,5 dioxybenzophenone. More of this material separated upon dilution with several volumes of water. The resulting yellow suspension was allowed to stand for an hour and then filtered. The clear filtrate was about saturated with potassium chloride,

whereupon the potassium salt of the thiosulfuric acid began to separate out as light yellow crystals. These were filtered off, washed with 5% potassium chloride solution, water, and then alcohol. Weight of dry product, 6 g. Recrystallization from hot water by salting out as before with potassium chloride and washing in the same manner gave bright crystalline flakes with a faint yellowish tint. The product decomposed near 240° without melting. Yield 5.1 g., or 60%.

It was insoluble in the ordinary organic solvents, but could be recrystallized from a large volume of alcohol. The solubility in cold water was slight, but increased considerably with temperature. Concd. sulfuric acid changed the crystals to a red color, and dissolved them slowly to give an orange solution. The potassium salt was apparently stable in 2 N sulfuric acid. It dissolved in .5 N alkali to give an orange solution. Chemical properties and analysis indicated the formula assigned. The potassium was determined as the sulfate by an adaptation of the method of Pregl.[30] Sulfur was determined by Carius' method.

Analysis: Calc. for $C_{13}H_9O_6S_2K$, C, 42.83% ; H, 2.49% ; K, 10.73% ; S, 17.51%.

Found C, 43.21% ; H, 2.40% ; K, 10.49% ; S, 17.53%.

The above thiosulfuric acid derivative was treated with an equal weight of 2-amino-5-dimethylaniline thiosulfuric acid in 20% sodium carbonate and oxidized by air, after an adaptation of a combination of a patented method [19] and the method of Heller, Quast, and Blanc[29] for making brilliant alizarin blue. These authors stated that the thiosulfuric acid of p-quinone did not give a single product when so condensed, and we found similarly that the product here consisted mainly of deep reddish violet crystals mixed with a bluish black amorphous substance. The violet crystals were soluble in glacial acetic acid, acetone, and nitrobenzene giving a bluish color, and in benzene giving a reddish violet.

The fact that a violet dye was formed above, indicated that the benzoyl and thiosulfuric acid groups were not on adjacent carbon atoms in our thiosulfuric acid derivative.

Hydroquinol dibenzoate

A method similar to that of Doebner and Wolff [1] was used for the preparation of this compound. .5 mole of hydroquinol was dissolved in 1 mole of benzoyl chloride on the steam bath and the mixture was heated until the evolution of hydrogen chloride ceased. The congealed mass was dissolved in boiling toluene. Upon cooling large flat needles separated out, which were filtered off, washed with hot alcohol, and dried. M.P. 204°, corr. Doebner and Wolff give 199°. Yield, 140.5 g., or 90%.

Dibenzoyl hydroquinol

This compound was prepared according to a slight, but important, modification of the method very briefly described by Doebner and Wolff.[1] 50 g. of hydroquinol dibenzoate was dissolved in 49 g. of benzoyl chloride as the temperature was brought to 200°. The mixture, maintained at 200°—205° by means of a metal bath, was treated with small quantities, not over .5 g. of finely ground anhydrous aluminum chloride at intervals sufficient to insure a continual, slow evolution of hydrogen chloride. After 48 hours the reaction was practically complete. The mixture appeared as a black charred viscous liquid, which turned to a resinous mass on cooling. 300 cc. of 15% alcoholic potassium hydroxide was next added, and the mixture heated at the boiling point for about 2 hours. The alcohol was now evaporated, and the residue treated with water and filtered. The blood red filtrate when saturated with carbon dioxide precipitated out the hydroquinol mixed with brownish colored impurities, which were essentially aluminum compounds. The precipitate was filtered off, washed with water and 1 N hydrochloric acid, and dried. Weight of crude product 8 g. Several recrystallizations from alcohol, with Norite, gave fine yellow needles which melted at 210.5°—211.1°, corr. Yield 12—15%. Doebner[2] gives 206° from alcohol and 207° from toluene.

Attempts to improve the yield of this product were made with particular aim of decreasing the charring. When the reaction was carried out at either 165°—175° or 175°—185° the

charring was increased and not more than a trace of the diketo derivative was formed. Anhydrous ferric chloride was used with and substituted for aluminum chloride, but produced little or no effect. Benzoyl chloride was heated with anhydrous aluminum chloride for several hours at temperatures near 170°, since Böeseken[17] reported that the former substance was decomposed by the latter above 170°. It was found that temperatures as low as 160° gave considerable decomposition, so this observation was taken as an explanation, at least in part, for the above charring effects.

The use of a high boiling solvent as nitrobenzene in view of preventing the decomposition seemed to hinder the condensation to such an extent that no diketo derivative was obtained.

.1 mole of 2,5 dimethoxybenzophenone in 10 cc. of carbon disulfide was treated with an equimolecular portion of benzoyl chloride and anhydrous aluminum chloride in view of introducing a second benzoyl group into the nucleus. The mixture was allowed to stand for 24 hours at room temperature and then heated at 50°—60° for 3 hours. The mixture was worked up in the usual manner, but no dibenzoyl substitution product was obtained. The main product isolated was 2 oxy, 5 methoxy benzophenone. M.P. 84°—85.5°, corr.

A small amount of monobenzoyl p-quinone was dissolved in excess benzaldehyde and exposed to sunlight in accordance with the method of Klinger and Standke[7] for producing 2,5 dioxybenzophenone from p-quinone. After several days of standing the mixture became quite dark but no crystalline material separated as in the experiments of these workers. Since the method even appeared exceedingly impractical for obtaining their product, and since the present adaptation did not offer conditions as favorable, the hope to prepare dibenzoyl hydroquinol in this manner was dropped.

Dimethyl ether of dibenzoyl hydroquinol

2 g. of dibenzoyl hydroquinol was dissolved in 40 cc. of 20% sodium hydroxide, and then 10 cc. of methyl sulfate was added gradually, with constant agitation and cooling. Toward the end of the addition, the temperature was allowed to rise to

about 50°. The original blood red solution changed to a distinct yellow. A yellowish white precipitate separated, which was filtered off after the excess methyl sulfate was decomposed with more alkali on the steam bath. Recrystallization from alcohol or glacial acetic acid gave colorless, dendritic flakes, which melted at 124°—124.5°, corr. Yield was about quantitative.

The product was insoluble in cold and hot 10% sodium hydroxide. The ether was readily reduced to the original hydroquinol by heating with 2 parts of constant boiling hydriodic acid and 1 part of glacial acetic acid for ½ hour.

Analysis: Calc. for $C_{22}H_{18}O_4$, C, 76.26%; H, 5.24%.
Found C, 75.61%; H, 5.08%.

Attempts to prove structure of dibenzoyl hydroquinol

(1) Unsuccessful reduction to the dihydrol. — .75 g. of dibenzoyl hydroquinol was covered with 50 cc. of water, and 10 g. of 3% sodium amalgam was added. This mixture was allowed to stand several hours, as in the reduction of p-benzoyl phenol to benzhydryl phenol carried out by Doebner.[2] A strong odor of benzaldehyde was soon present. The original blood red solution darkened slowly to a brownish black. The mixture was filtered into water, whereupon a small amount of grayish powder separated, which indicated the original ketonic linkage to have suffered rupture.

The use of glacial acetic acid as the solvent in the above reduction prevented the decomposition from giving benzaldehyde, but the reaction worked exceedingly slowly even in the hot. Only a small quantity of changed product was isolated, which softened and decomposed over a large range when a melting point determination was attempted.

Since alkaline reduction was more likely to give the dihydrol without pinacone formation, alkaline reduction was repeated on the methylated product of dibenzoyl hydroquinol in view of blocking the hydroxyl groups and thus eliminating the possibility of forming benzaldehyde. No odor of benzaldehyde was detected when the reduction was carried out with 3% sodium amalgam in hot alcohol, according to an adaptation of

the method of Perrier and Caille,[20] which consisted of heating with 5% sodium amalgam in alcohol at about 60° for 30 hours. A clear, colorless oil was obtained here, which became semi-granular when chilled. All common solvents and mixtures failed to give rise to a crystalline product in attempted recrystallizations. Trials to form a solid ester by means of the Schotten-Baumann method, using p-nitrobenzoyl chloride and benzoyl chloride were unsuccessful.

(2) Fusion with alkali.—Due to the limited amount of material it was hoped to be able to convert the benzoyl groups into other groups in view of obtaining directly a known product. Doebner[2] changed p-benzoyl phenol to p-hydroxybenzoic acid by fusion with alkali. However, dibenzoyl hydroquinol decomposed instantly when subjected here to similar treatment.

(3) Bromination.—Refluxing with a slight excess of bromine in glacial acetic acid gave a low melting, brominated product, from which no homogeneous material could be obtained for further study. A similar trial was made by heating only for an hour on the steam bath followed by long standing at room temperature. An exceedingly small amount of a bromo derivative resulted after tedious recrystallization of the product from 50% alcohol. M.P. 220°, corr. Further study of the product was not made due to want of material. When chloroform or carbon tetrachloride were used as the solvent in the above bromination, no appreciable action took place after several hours.

A trial to effect the bromination through the addition of bromine to dibenzoyl p-quinone was also unsuccessful. .5 g. of the quinone in 5 cc. of chloroform was treated with .24 g. of bromine in 5 cc. of the same solvent. The mixture was allowed to stand one hour. The chloroform and slight excess of bromine was evaporated off slowly under diminished pressure. The orange colored residue was recrystallized from alcohol to give a product that melted at 210°—211°, corr. A mixed melting point indicated the substance to be essentially dibenzoyl hydroquinol, although the Beilstein test was faintly affirmative for halogen. The mother liquor from the crystal-

lization was diluted with water, whereupon a red oil separated, which contained substituted bromine. A homogeneous product could not be isolated from this oil.

Dibenzoyl p-quinone

A solution of 4 g. of dibenzoyl hydroquinol in 75 cc. of warm glacial acetic acid was added drop-wise over a period of a half hour to a mixture of 10 g. of sodium dichromate and 10 cc. of concd. sulfuric acid in 250 cc. of water. The mixture was stirred mechanically during the addition and for 10 minutes after. The suspended, finely divided product was filtered off, washed well with water, and dried. The light tan powder weighed 3.6 g. and melted 160°—163°, corr. Recrystallization from a large volume of ligroin (B.P., 100°—108°) gave orange needles, melting at 164—164.5°, corr. Yield, 2.3 g., or about 60%. The heat necessary to effect solution during the recrystallization seemed to be harmful to the product, leaving behind some brownish colored insoluble material.

The quinone was soluble in most of the common organic solvents, and moderately so in hot water to which it imparted a reddish orange color. It was much more stable toward alkali than the previously described monobenzoyl p-quinone. Alkaline permanganate oxidized it easily to benzoic acid in the cold. Chromic acid likewise gave benzoic acid, but a much longer time was required. The results of the action with hydroxylamine were much the same as those already described in detail for monobenzoyl p-quinone, indicating it to be also a good oxidizing agent. The quinone was readily reduced to the original hydroquinol by means of sulfurous acid. Chemical properties and analysis indicated it to be dibenzoyl p-quinone.

Analysis: Calc. for $C_{20}H_{12}O_4$, C, 75.93%; H, 3.83%.
Found C, 75.80%; H, 3.94%.

Monoanilido dibenzoyl hydroquinol

.45 g. of dibenzoyl p-quinone in 20 parts of warm glacial acetic acid was treated with .4 g. of aniline in 3 cc. of the same solvent. After a short time fine glistening plates began separating out from the dark solution. Thirty minutes was found to

be sufficient time to allow complete separation. Greenish yellow crystals resulted when filtered, washed with glacial acetic acid and then alcohol. Weight, .35 g. M.P., 234°—236°, corr. Recrystallization from alcohol gave fine, glistening yellow plates, which melted at 234.9°—236.8°, corr., after having changed to a distinct orange shade at 10° below this point. Slight decomposition was also observed near 228°. Yield, .3 g., or 52%.

The crystals dissolved slowly in cold dilute alkali, but quickly in the hot, to give a deep orange solution which changed gradually on cooling to a distinct yellow. Chemical properties and analysis indicated the formula assigned.

Analysis: Calc. for $C_{26}H_{19}O_4N$, C, 76.25% ; H, 4.68%.
Found C, 76.33% ; H, 4.66%.

Triacetate of dibenzoyl hydroxyhydroquinol

A method similar to the one already described for preparing the corresponding monobenzoyl derivative was used to prepare this compound. 1 g. of dibenzoyl p-quinone was introduced into 3 g. of acetic anhydride to which had been added 2 drops of concd. sulfuric acid. The orange solution after standing a few minutes at 40°—50° became a light yellow. The mixture was poured onto cracked ice in order to decompose the excess acetic anhydride without effecting the easily hydrolyzed triacetate. The light yellow oily product finally turned to a whitish solid, which when filtered, washed well with water, then 50% alcohol, and dried, weighed about 1.25 g. Recrystallization from alcohol gave white shiny flakes, which melted at 120°—120.5°, corr. Yield, .9 g., or 62%.

The crystals were insoluble in cold dilute alkali, but soluble in the hot due to hydrolysis, giving an orange solution. Chemical properties and analysis indicated the formula assigned.

Analysis: Calc. for $C_{26}H_{20}O_8$, C, 67.79% ; H, 4.38%.
Found C, 67.85% ; H, 4.44%.

Dibenzoyl hydroxyhydroquinol

A mixture of .5 g. of the above triacetate dissolved in 5 cc. of alcohol to which .5 cc. of concd. hydrochloric acid had

been added was heated for one hour on the steam bath. The resulting deep yellow solution was diluted with an equal volume of water, whereupon fine needles formed on cooling. Yield of crude product was almost quantitative. M.P. 193°—194.5°, corr. Recrystallization from 50—60% alcohol gave rosettes of yellow needles, which melted at 196.9°—197.5°. Yield, .3 g., or 83%.

The product dissolved in dilute alkali to give an orange colored solution, which was quite stable toward air oxidation, precipitating out the original material upon acidification after standing for a few minutes.

Analysis: Calc. for $C_{20}H_{14}O_5$, C, 71.83%; H, 4.22%.
Found C, 71.47%; H, 4.21%.

Some oxidation-reduction relations of the acyl p-quinones and hydroquinols

(1) Reduction of mono- and dibenzoyl p-quinones.—Glacial acetic acid solutions of each quinone, having equimolecular concentrations, were mixed with saturated sulfurous acid under identical conditions. Each quinone was reduced to its corresponding hydroquinol, but more complete and rapid reduction took place in the case of the dibenzoyl derivative, which indicated that the latter substance possessed the greater affinity for hydrogen, and therefore might be expected to have the higher reduction potential.

(2) Acid oxidation of the hydroquinols.—The treatment of these substances with dilute chromic acid mixture also brought out a marked difference in the ease of oxidation of each, which ran parallel with the findings in (1). The method already described for preparing monobenzoyl p-quinone in almost quantitative yields when applied as such to produce dibenzoyl p-quinone from its corresponding hydroquinol, gave very incomplete oxidation and much of the original hydroquinol was recovered from the product.

(3) Alkaline oxidation of the hydroquinols.—Dilute, blood red alkaline solutions possessing equimolecular concentrations of mono- and dibenzoyl hydroquinol respectively, were exposed to air for a short time and then acidified by dilute min-

eral acid. The yellow hydroquinol was precipitated unchanged in each case. However, when the blood red solutions were exposed to air for a sufficient period the solution of monobenzoyl hydroquinol turned a dark brown, while the other solution retained its original color. Acidification now of each solution precipitated only the dibenzoyl hydroquinol unchanged. When the same solutions were not allowed free access to air, both were quite stable over the same period of time as used above. Thus the dibenzoyl derivative appeared much more stable toward alkaline oxidation. Similar indication was gathered when equivalent quantities of hydrogen peroxide was used as the oxidizing agent. Dark brown solutions formed in each case, but the alkaline dibenzoyl hydroquinol retained its blood red color over a much longer period of time. A flocculent, light brown precipitate formed upon acidification, from which benzoic acid was the only product isolated. It was quite possible that p-quinones were formed as intermediate products, but due to the beta diketone grouping present in the molecule might be expected to be unstable toward an alkaline oxidizing medium to give rise to benzoic acid. The intermediate quinones could not be isolated, so no further light was thrown on the above reactions.

Experimental Dyeings with the Acyl p-Quinones

A piece of unbleached wool was heated in a 3% solution of monobenzoyl p-quinone in glacial acetic acid on a steam bath for ½ hour. The wool assumed a dark reddish color, whereas the solution retained its yellowish orange color. The dyed cloth was washed well with warm glacial acetic acid, then hot water, and dried. A reddish brown shade resulted, which was quite fast to washing and acid, but much less to light, fading to a yellowish brown after three days of exposure to sunlight. It was not fast to stoving, bleaching, or alkali, turning to a dark brown in the case of the latter, due in part at least to the fibre being attacked by the alkali.

The above experiments repeated with dibenzoyl p-quinone gave similar results. The shade produced, however, was more reddish, but less intense and somewhat less fast.

Since dianilido monobenzoyl p-quinone was a highly colored body and unusually stable toward alkalies, acids, and other reagents, attempts were made to precipitate this substance within the fibre. A piece of unbleached wool was treated with a 5% solution of monobenzoyl p-quinone, the impregnated wool was then treated with aniline in glacial acetic acid. The cloth turned a reddish shade, but the intense red color appeared chiefly in the solution even after 1 hour of warming on the steam bath. Other similar trials were made to form the colored product within the fibre, but the depth and quality of the color were found in no case to be satisfactory. Evidently the amino group of the wool fibre was not allowed to fix the quinone when in the presence of the more active amino group in aniline.

Fastness of all of the dyeings made above was determined by the tests advocated by Cain and Thorpe[26].

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